

HETEROSTRUCTURE SEMICONDUCTOR DEVICES

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Inventor: VAN VECHTEN JAMES A; WOODALL JERRY M

Applicant: IBM

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Abstract of CA1095154

Self-completing semiconductor materials may be converted to p-conductivity by charged particle irradiation which rearranges the atoms in the crystal lattice and may then be used in a heterostructure semiconductor device to permit the including in the device of materials with a wide range of new properties.

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(19) (CA) **CANADIAN PATENT** (12)

(54) HETEROSTRUCTURE SEMICONDUCTOR DEVICES

(72) Van Vechten, James A.;
Woodall, Jerry M.,
U.S.A.

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U.S.A.

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BACKGROUND OF THE INVENTION

2 The heterostructure semiconductor device is one in which
3 regions of different semiconductor materials are present in the same
4 device body. Usually the regions of the different semiconductor materials
5 are of opposite conductivity type and form a p-n junction at their inter-
6 face. There are a variety of useful advantages that are obtained from
7 such a structure. The advantages result from added flexibility in proper-
8 ties of materials, dimensional precision and processing. As an example
9 of the devices that have appeared in the art, the injection laser using a
10 double heterostructure illustrates the interrelated materials, structure
11 and processing advantages that are gained. In the double heterostructure
12 injection laser the central region of one semiconductor material and the
13 two regions of the other semiconductor material produce an electric field
14 at each interface which serves to confine injected carriers to the desired
15 region. At the same time the added flexibility of the different materials
16 permits selecting materials having an index of refraction at the inter-
17 faces such as to confine the light to the cavity region. The art has
18 been directed in its development toward many types of devices using hetero-
19 structure but one serious limitation which has heretofore existed has been



1 the fact that a large class of compound type semiconductor materials
2 that have very useful properties has exhibited a phenomenon known as
3 self-compensation and as a result the conductivity is always one type,
4 usually N.

5 REFERENCE TO RELATED APPLICATION

6 In our copending application Serial No. 282,753 filed
7 August 10, 1976 the ability to impart -p- conductivity to self-
8 compensated compound semiconductor materials is set forth. This
9 ability now opens up to device use an entire class of compound semi-
10 conductor materials with a wide range of physical properties.

11 SUMMARY OF THE INVENTION

12 Heterostructure semiconductor devices are fabricated by forming
13 a region of a self-compensated compound semiconductor material on a body
14 of semiconductor material and then depending on the device requirements
15 imparting -p- conductivity as needed. In accordance with the invention,
16 heterostructures of two and more contiguous regions for various device
17 structures may be fabricated.

18 The principal object of the invention is to set forth hetero-
19 structures, one region of which, is made of self-compensated compound
20 semiconductor material, all useful in fabricating semiconductor devices.

21 DESCRIPTION OF THE DRAWING

22 FIG. 1 is a view of a heterostructure body with two regions
23 one of which is a self-compensated compound semiconductor.

24 FIG. 2 is a view of a self-compensated compound semiconductor
25 double heterostructure body.

1 FIG. 3 is a sketch of a self-compensated double heterostructure
2 injection laser.

3 DETAILED DESCRIPTION

4 The phenomenon of self-compensation in compound semiconductor
5 materials results in the conductivity being always one type, usually N,
6 so that materials exhibiting this phenomenon heretofore were very res-
7 tricted in their device usefulness. While the phenomenon and how to
8 overcome it are set forth in detail in our referenced copending application
9 Serial No. 282,753 filed August 10, 1976 the following is a generalized
10 description.

11 The phenomenon occurs where one element of the material generates
12 enough lattice defects, commonly vacancies to compensate any concentration
13 of impurities of the desired conductivitytype. In practice the phenomenon
14 has been observed to prevent p-type conductivity in large bandgap semi-
15 conductors where anion vacancies are more numerous than cation vacancies.
16 If the fermi level in this type of material is located near the valence
17 band with a significant energy separation from a higher level which is the
18 donor ionization energy level, then the total energy of the material could
19 be lowered by generating an anion vacancy ionizing same to its donor state.
20 and allowing the resulting electron to drop to the fermi level. This
21 process would allow the fermi level to rise away from the valence band
22 quenching p-type conductivity. This invention provides structures employing
23 "p-type" conductivity in these materials.

24 Referring to FIG. 1 a heterostructure body is shown having a
25 region 2 of a conventional semiconductor material and a region 3 of a
26 self-compensated semiconductor material forming a p-n junction 4 with the
27 region 2. Electrodes 5 and 6 are applied to regions 2 and 3, respectively,
28 for device applications standard in the art.

1 The ability to provide both n-type and p-type conductivity to
2 the self-compensating compound semiconductor material region 3 permits
3 a wider relaxation of conductivity type and resistivity of the region 2.

4 As an example of a heterostructure of the invention the region
5 2 could be made of gallium nitride (GaN) and the region 3 could be made
6 of aluminum nitride (AlN). The conversion to p-type conductivity is
7 accomplished by irradiation with charged particles. These particles may
8 be electrons, protons or ions. This may be contrasted with normal ion
9 implantation used to convert conductivity-type wherein the concentration
10 of implanted impurities overwhelms the concentration of existing impurities.
11 This is accompanied by a large amount of crystal damage which must be
12 annealed out to reveal the effect of the doping level. The ion implantation
13 technique produces wide junctions.

14 In other words the invention rearranges the crystal atoms to
15 produce conductivity whereas ion implantation relies on implanted atoms for
16 control conductivity. The resulting structure has a bandgap in the region
17 2 of approximately 3.39eV and a bandgap in region 3 of approximately 6.2eV.

18 The device may be fabricated by first providing the region 2 of
19 gallium nitride using the technique set forth by H. Maruska and J. Tietjen
20 in Applied Physics Letters, Vol. 15, No. 10, November 15, 1969 and para-
21 phrased as follows:

22 A straight tube is provided through which the pertinent gaseous
23 species flow to provide chloride transport of metallic gallium, and subse-
24 quent reaction of these transport products with ammonia to form GaN on a
25 substrate surface of single crystal sapphire (Al_2O_3). Since the region 3
26 will be (AlN) a 111 crystallographic orientation is preferably used. The
27 sapphire substrates are mechanically polished to a flat mirror-smooth finish,
28 and then heat-treated in hydrogen at 1200°C, prior to their introduction to

1 the growth apparatus. Typical substrate dimensions are about 2 cm² in
2 area and about 0.25 mm thick. In the growth procedure, freshly heat-
3 treated substrates are inserted into the deposition zone of the growth
4 chamber and heated in hydrogen at a rate of about 20°C/min. When the
5 final growth temperature is reached, the NH₃ flow is started and, after
6 a 15-min. period to allow the NH₃ concentration to reach a steady-state
7 value, the HCl flow is started to provide transport of the Ga and deposition
8 of GaN.

9 The flow rates of pure HCl and NH₃ are about 5 and 400 cm³/min,
10 respectively, and an additional 2.5 liters/min of hydrogen is used as a
11 carrier gas.

12 The conductivity of region 2 is n-type. Further, GaN other than
13 n-type is not readily produced.

14 The region 3 of self-compensated semiconductor material is next
15 applied. In the example of aluminum nitride (AlN) the region 3 is formed
16 on the above-described region 2 by the technique set forth by R. F. Rutz in
17 Applied Physics Letters, Vol. 28, No. 7, April 1976. The technique is para-
18 phrased as follows:

19 A 1-μm-thick layer of AlN is grown on region 2 by rf reactive
20 sputtering at 1000 C. This layer, serves as a nucleating seed for a
21 growth procedure carried out by placing the AlN-coated GaN region 2,
22 AlN face down on a polycrystalline sintered AlN source wafer, in a
23 tungsten crucible heated to ~ 1850 C in a 15% H₂, 85% N₂ forming gas
24 atmosphere. A vertical temperature gradient promotes the transfer of
25 the AlN from the sintered source to the substrate forming epitaxial
26 single-crystal layers.

27 The AlN region 3 is n-type conductivity because of the self-
28 compensating phenomenon that is the nature of the AlN material. The region
29 3 is now converted to p-type conductivity by bombardment with protons (H⁺)

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1 or, depending on the desired resistivity, by the combination of the
2 introduction of an acceptor impurity such as beryllium (Be) and
3 ionized beryllium (Be^+) bombardment as set forth in the referenced co-
4 pending application. The depth of conversion establishes the location
5 of the p-n junction. The resulting heterostructure is useful as an
6 asymmetric conducting device or electrical to light conversion and detection
7 device when electrical signals are applied to terminal 5 and 6 or light
8 detection device when light is absorbed by region 1.

9 Referring next to FIG. 2 a view is provided of a double hetero-
10 structure body 10 wherein regions 11 and 12 are made of a self-compensated
11 compound semiconductor material and form p-n junctions 13 and 14, respect-
12 ively, with a region 15 of a semiconductor material of opposite conductivity
13 type. The electrodes 16 and 17 are provided for device use. The conductivity
14 assignments of n and p are made merely to facilitate explanation and are
15 not governed by material requirements because in accordance with the in-
16 vention both n and p self-compensated compound semiconductor regions can
17 be fabricated in heterostructures.

18 The structure of FIG. 2 may be used as a high temperature trans-
19 istor, an optical modulator, a light emitting device or an injection laser
20 by application of signals to and via the electrodes 16 and 17.

21 The heterostructure of FIG. 2 using AlN for regions 11 and 12
22 and GaN for region 15, may be fabricated by growing as set forth by Rutz
23 cited above, the region 11 of AlN on a 111 crystallographic orientation
24 substrate of Tungsten (W) or aluminum oxide (Al_2O_3) a 1m thick layer by
25 reactive rf sputtering at 1000°C. This layer serves as a nucleating seed for
26 a growth procedure carried out by placing the AlN coated substrate face down
27 on a polycrystalline sintered AlN source wafer in a tungsten crucible heated
28 to ~ 1850 ~ °C in a 15% H_2 , 85% N_2 forming gas atmosphere. A vertical tempera-

1 tude gradient promotes transfer of the AlN from the sintered source to the
2 substrate in an epitaxial layer.

3 The region 15 of gallium nitride (GaN) is then formed on the
4 region 11 as set forth by Maruska et al cited above. Chloride transport is
5 used for metallic gallium with subsequent reaction of the transport products
6 with ammonia to deposit (GaN) on the region 11 serving as the substrate. The
7 GaN material formed is n-type. The flow rates of pure HCl and NH_3 are about
8 5 and 400 cm^3/min , respectively, and an additional 2.5 liters/min of hydrogen
9 is used as a carrier gas. With these flow rates, a substrate temperature of
10 825°C , a Ga-zone temperature of 900°C , and a center zone (that region
11 between the Ga and deposition zones) temperature of 925°C , growth rates
12 of about 0.5 μ/min are obtained under steady-state conditions. Typical
13 thicknesses for the deposit for region 15 are in the range of 50-150 μ .
14 Doping is accomplished, during the growth process, by introducing the dopant
15 to the growth apparatus, either as its hydride or by direct evaporation of
16 the element into a hydrogen-carrier gas.

17 The region 12 is next grown using the technique set forth above
18 for region 11.

19 Since both regions 11 and 12 are normally n-type it is next
20 necessary to remove the body 10 from the substrate and convert to p-type.
21 This is done by either charge particle irradiation or by a combination of
22 acceptor implantation and bombardment as set forth in the referenced co-
23 pending application.

24 A double heterostructure is next shown fabricated into an in-
25 jection laser device. In this type of device electrical energy is converted
26 to light energy in a region that is designed to simultaneously keep carrier
27 density high and photons confined. In accordance with the invention the
28 flexibility of being able to include the class of self-compensating compound

1 semiconductor materials in both conductivity types permits inclusion in
 2 the structure of many wider bandgap materials and better index of refrac-
 3 tion matches than heretofore in the art. In this type of device it is
 4 desirable that the cavity wherein the carrier population inversion is to
 5 occur be of a bandgap such that light of the desired frequency is produced
 6 and that the bandgap is lower than the outside regions. For efficiency,
 7 it is desirable that the cavity be small enough for high carrier concentra-
 8 tion at low current and that the cavity have a higher index of refraction
 9 than the outside regions. In accordance with the invention this double
 10 heterostructure injection laser need have only one p-n junction.

11 Referring to the injection laser of FIG. 3 the device consists
 12 of a body 20 mounted on a conducting substrate 21. The body 20 is made
 13 up of a region 22 of one conductivity type, for example n, of a for example,
 14 self-compensated compound semiconductor material. The body 20 also contains
 15 a region 23 of a semiconductor selected for its bandgap, and index of
 16 refraction. Since the conductivity type of this region 23 may be the same
 17 as 22, for example n, substantial material selection flexibility has been
 18 provided. The body 20 has an outer layer 24 of self-compensated semicon-
 19 ductor material of p conductivity type forming a p-n junction 25 with the
 20 region 23. Electrodes 26 and 27 are applied to regions 21 and 24, respect-
 21 ively, for electrical signal purposes. A fabry-Perot interferometer is
 22 formed by making faces 28 and 29 parallel.

23 Since it is desirable that the bandgap be higher in the regions
 24 22 and 24 than in the region 23 and that the index of refraction be lower
 25 in the regions 22 and 24 than in the region 23, the self-compensated
 26 compound semiconductor material aluminum nitride (AlN) may be employed, for
 27 example in regions 22 and 24, together with for example, the semiconductor
 28 material gallium nitride (GaN) or gallium ₁₋₄ aluminum _x nitride ($\text{Ga}_{1-x}\text{Al}_x\text{N}$).

The device should preferably have dimensions of regions 22 and 24 in the range of 0.1-5 microns. The thickness of the region 23, the cavity should be in the range of 500 to 5000Å. The substrate contact 21 should be aluminum (Al) and the contact 27 should have a large work function and be beryllium (Be) or gold (Au). The Fabry-Perot faces 28 and 29 may be rendered parallel by the standard techniques of cleaving or polishing.

The region 22 is formed according to the technique set forth by R. F. Rutz cited above and paraphrased as follows:

First epitaxially deposit a 1μ thick layer of aluminum nitride (AlN) on 111 crystallographic orientation single crystal tungsten (W) or sapphire (Al_2O_3) by rf reactive sputtering at 1000°C. This layer serves as a nucleating seed for further growth where the AlN is placed face down in contact with an AlN sintered source wafer in a tungsten crucible heated to ~ 1850°C in a 15% H_2 , 85% N_2 forming gas atmosphere. A vertical temperature gradient promotes the transfer of the AlN and is continued until the range of 1 to 5 microns is achieved. This AlN will be n-type because of vacancy self-compensating on the region 22 as a substrate.

The region 23 is formed using the material gallium nitride (GaN) as an example, using the technique set forth by Maruska et al cited above and paraphrased as follows:

Chloride transport of metallic gallium is reacted at the deposition site with ammonia (NH_3) to form gallium nitride (GaN) on the region 22 substrate. The flow rates of HCl and NH_3 are 5 and 400 cc/min, respectively and an additional 2.5 liters/min if hydrogen is used as a carrier gas. The gallium zone temperature is 900°C, the region 22, temperature is 825°C and the region between the gallium source and the substrate is 925°C. These conditions produce growth rates of about 0.5 μ/min and is continued until 500-5000Å are grown. The conductivity type of the GaN material produced is N.

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The region 24 is next formed using the technique for region 22 using the body now made up of regions 22 and 23 as the substrate. Some beryllium (Be) as a future p-type impurity source may be included in this step. The region 24 is grown between 0.1 and 5 microns thick. The region 24 is then converted to p-type conductivity type. A beryllium (Be) coating is placed on region 24 and a beryllium ion source in standard ion implantation techniques is employed to introduce beryllium. The beryllium (Be^+) bombardment takes place at 140 kilowatts. The beryllium (Be) coating can then serve as part of electrode 27. The substrate of aluminum oxide (Al_2O_3) or tungsten (W) is replaced by an electrode 26 of aluminum. It should be noted that the fabrication is arranged so that high temperature processing steps are minimized after the p-type conversion.

It should be understood that the above-described arrangements are illustrative of many possible specific embodiments that will be clear to one skilled in the art in the light of the invention.

FIG. 1

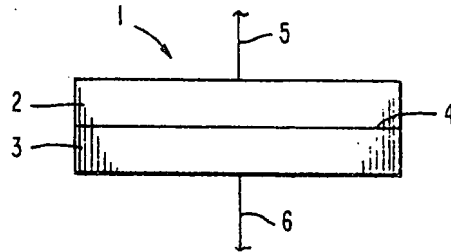


FIG. 3

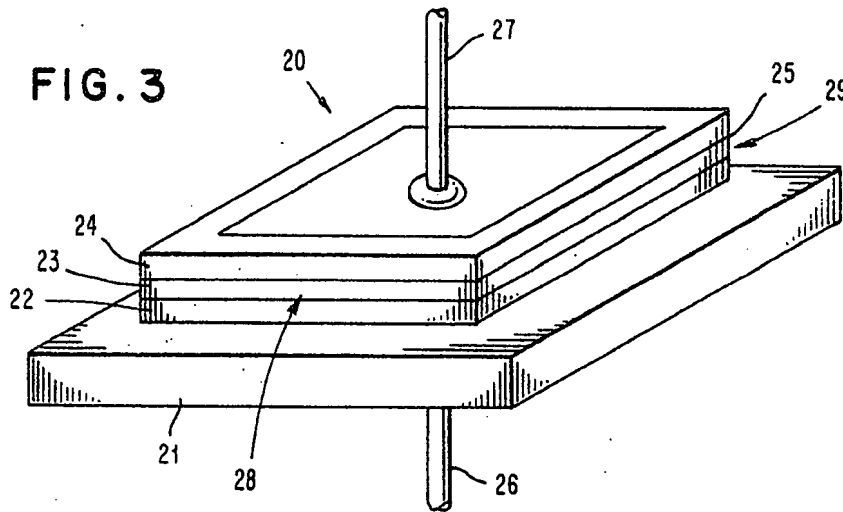


FIG. 2

